

## **PRELIMINARY STUDIES ON MALEATED POLYETHYLENE-OCTENE ELASTOMER MODIFIED POLYAMIDE 6 / POLYPROPYLENE (70:30) NANOCOMPOSITES**

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### **ABSTRACT**

Rubber toughened nanocomposites consisting of polyamide 6 (PA6) and polypropylene (PP) matrix (70:30) with a maleated polyethylene-octene elastomer (POEgMAH) and organophilic modified montmorillonite (MMT) were prepared by melt compounding in a co-rotating twin-screw extruder followed by injection moulding. The POEgMAH content was varied in the range of 0 wt% - 20 wt% and the weight fraction of organoclay was fixed at 4 wt %. Mechanical properties of the blends were investigated by tensile, flexural and Izod impact testing. X-ray diffraction (XRD) was used to characterise the nanocomposites. Izod impact measurements indicated that the addition of POEgMAH led to a significant improvement in the impact strength of the PA6/PP nanocomposites. The impact strength increased up to more than twice enhancement after addition of 15wt% POEgMAH into PA6/PP nanocomposites. However, the tensile and flexural properties were found to decrease with increasing concentration of POEgMAH. XRD revealed that an intercalation organoclay silicate layer structure was formed in rubber toughened PA6/PP nanocomposites.

### **Keywords**

Polyamide 6/polypropylene, blends, nanocomposites, polyethylene octene elastomer, toughened polymers and mechanical properties

### **INTRODUCTION**

Polymer nanocomposites have attracted great interest in most recent researches. Nanocomposite exhibit superior properties such as enhanced stiffness and strength reduced gas permeability and improved flame retardancy. Polymer clay nanocomposite based on single polymer matrix have been extensively studied by numerous researchers [1-5]. However, more recently thermoplastic nanocomposites based on blends of two or more polymeric materials such as binary or ternary blends [6-8], seem to be the new approach in the nanocomposites studies.

In a previous study, the elastic modulus of polymer and blends increases significantly in the presence of 5-10wt% nanoclay [2]. Based on tensile and flexural strength the optimum loading of organoclay was found to be 4 wt%. A further increase in organoclay content, would not increase the modulus significantly because it is difficult for the organoclay to dispersed at higher loading especially using melt intercalation approach [6,7].

Polymer blending is an economic route for getting new polymer materials at low cost and combining the performance of the corresponding neat polymers. In recent year, there has been much interest in the development of polymer blends based on engineering polymer such as polyamide (PA) with polyolefin [6-9]. Polyamide 6 (PA6) plastics are wide engineering application due to their easy processing, low friction, wear resistance, and high melting temperature. However, PAs are limited by its higher cost and higher affinity for water and its mechanical properties are often significantly affected by the absorption of water. It is also known

to be a notch-sensitive thermoplastic owing to a markedly lower resistance to crack propagation than to crack initiation. Polypropylene (PP) has good overall mechanical performance, good moisture resistance and low cost but it shows relatively poor chemical and heat resistance. Thus, PA6 is frequently blended with the PP, when it properly compatibilized can potentially offer a wide range of desirable characteristic such as good chemical resistance, lower water absorption and reduced cost [10].

However, one of the major drawbacks of PA6 and PP as well as their blends is its low impact strength particularly at low temperature. Hence, toughening of both PA6 and PP with elastomeric materials has become important where high impact resistance is necessary. Ethylene-propylene rubber (EPR), ethylene propylene-diene monomer rubber (EPDM) and styrene ethylene butylenes styrene block copolymers (SEBS) are commonly used PA6/PP blends impact modifiers [9,11,12].

In this study, polyethylene octene copolymer (POE) a novel polyolefin elastomer developed using a metallocene catalyst by the Dow Chemical Co was used. Compared with the conventional polyolefin elastomer EPDM, POE typically exhibit faster mixing and better dispersion [10]. Therefore, an attempt was made to substitute EPDM with POE elastomer to achieve high toughness. Semicrystalline PA6 and POE rubber are highly incompatible, they require some means to improve compatibility between them. Thus, POE modified by grafting with maleic anhydride was used. This functionalized polymer copolymerize 'in situ' by grafting with PA6, giving rise to the interfacial adhesion between the rubber and the PA6, which are believed to be essential for promoting toughness. Maleated olefinic rubber mostly utilized as an impact modifier for PA6. Therefore it is a primary choice for impact modification of PA6/PP blends. In addition, these reactive rubbers are the affinity of the olefinic rubber for PP.

This paper focuses on the effects of the POEgMAH content on the mechanical and morphology of PA6/PP nanocomposites.

## MATERIALS AND METHODS

### Materials

The blends used in this work are described in Table 1. The PA6 (Amilan CM 1017) was a commercial product from Toray Nylon Resin AMILAN, Japan. The MFI of PA6 was 35 g/10 min at 230 °C and 2.16 kgf (21.2 N) and the density was 1.14 g/cm<sup>3</sup>. The PP (SM 240) was obtained from Titan PP Polymers, Johor Bahru, Malaysia. The melt flow index (MFI) and density of PP were 25 g/10 min (at 230 °C and 2.16 kgf (21.2 N)) and 0.9 g/cm<sup>3</sup> respectively. Maleated PP (PPgMAH) was Orevac CA 100 with ~1wt% of maleic anhydride (MA) produced by ATOFINA, France. Polyethylene-octene random (11 wt % octene) copolymer grafted with maleic anhydride (POEgMAH) (Fusabond MN493D), with density 0.87 g/cm<sup>3</sup> was supplied by DuPont Dow Elastomers, Wilmington, USA. The organoclay (Nanomer 1.30 TC) was a commercial product from Nanocor Inc, Arlington Height, USA. It was a white powder containing montmorillonite (MMT) (70 wt %) intercalated by octadecylamine (30 wt %).

	PA6	PP	PPgMAH	Organoclay	POEgMAH
PA6/PP/FA4/C5	63.7	27.3	5	4	-
PA6/PP/FA4/C5/E5	60.2	25.8	5	4	5
PA6/PP/FA4/C5/E10	56.7	24.3	5	4	10
PA6/PP/FA4/C5/E15	53.2	22.8	5	4	15
PA6/PP/FA4/C5/E20	49.7	21.3	5	4	20

**Table 1: Blends formulation**

### ***Compounding and test specimen preparation***

PA6, PP, PPgMAH, POEgMAH and organoclay were dry blended in a tumbler mixer according to the composition in Table 1. The polymers and additives were then melt blended by simultaneous addition of all components into a Berstoff (Hannover, Germany) co-rotating twin screw extruder. The barrel temperatures were gradually increased from hopper to die at 200, 220, 230 and 240 °C and the rotating screw was 50 rpm. Prior to extrusion, PA6 pellets were dehumidified by using a dryer at 80 °C for 8 hours. The pelletised materials were dried and injection moulded into the shapes required for standard tensile, flexural and impact specimens using a JSW (Muroran, Japan) Model N100B II injection moulding machine with a barrel temperature of 210-240 °C. All the specimens were allowed to condition under ambient conditions for at least 24 hours prior to testing.

### ***Mechanical Properties***

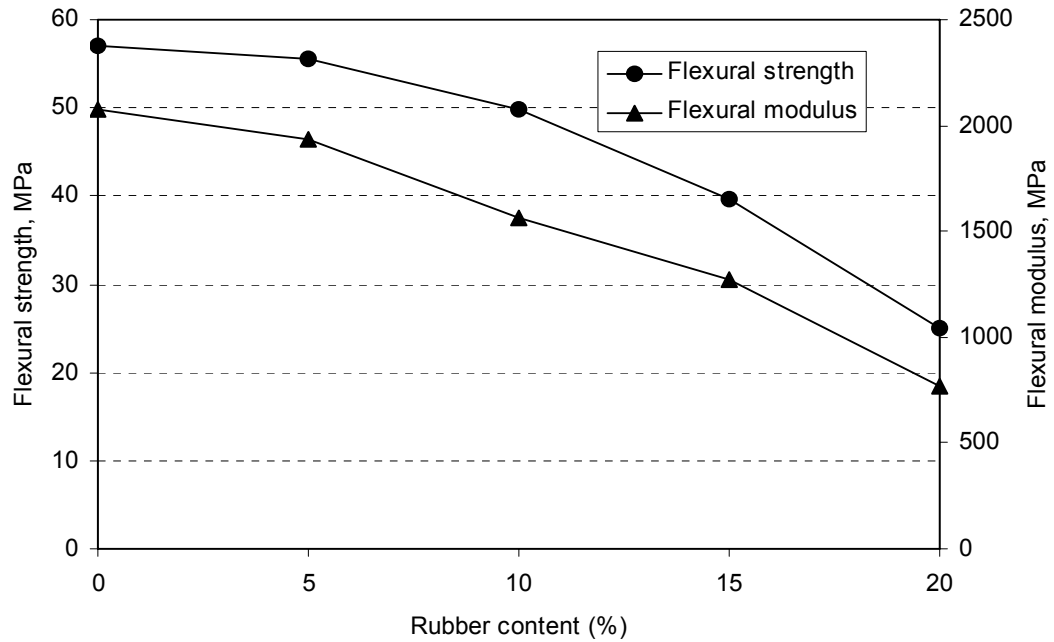
Tensile and flexural tests were carried out according to ASTM D638 and ASTM D790 respectively using an Instron (Bucks, UK) 5567 Universal Testing Machine under ambient conditions. The crosshead speed for tensile testing was 50 mm/min and for flexural tests it was 3 mm/min. The Izod impact tests were carried out on notched specimens using a Toyoseiki (Tokyo, Japan) impact tester under ambient conditions according to ASTM D256. The values reported in this study were the average of five values.

### ***X-ray diffraction (XRD)***

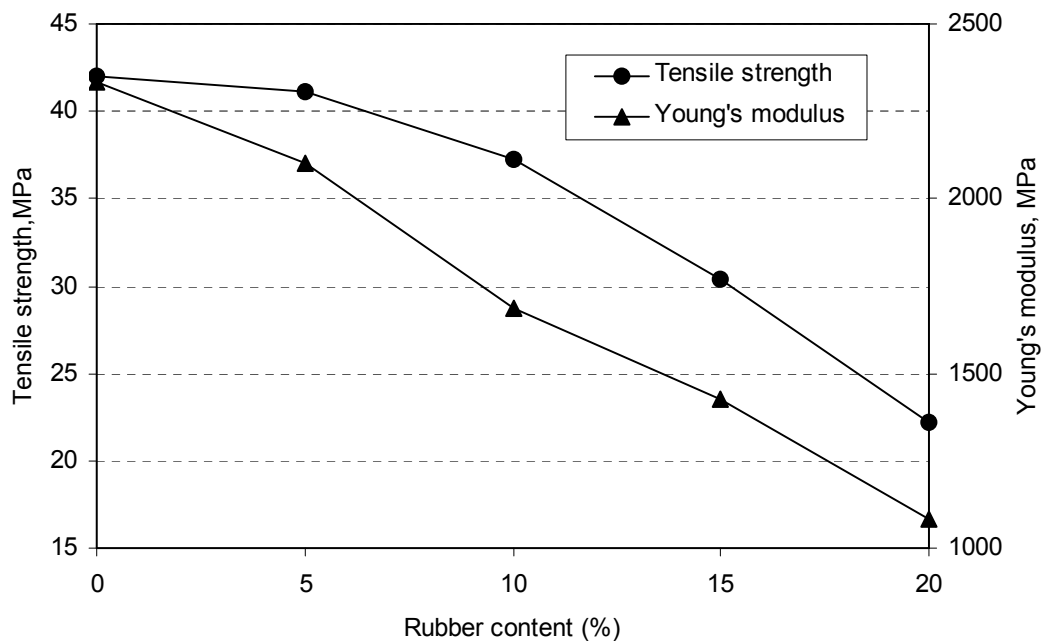
X-ray diffraction was performed with the Siemens (Berlin, Germany) D5000 X-Ray Diffractometer in order to confirm the formation of nanocomposites. The diffraction patterns were recorded with a step size of 0.02 ° from  $2\theta = 2$  to 10 °. The interlayer spacings of the organoclay in the nanocomposites were derived from the peak position (d001-reflection) in XRD scans according to the Bragg equation.

## **RESULTS AND DISCUSSION**

Figures 1 and Figure 2 show the Young's modulus, tensile strength, flexural modulus and strength as a function of rubber content for PA6/PP nanocomposites. It can be seen that tensile and flexural properties followed the same trend. The Young's modulus, tensile strength, flexural modulus and strength gradually decreased with increasing rubber. This is expected, as POEgMAH are low modulus materials. This observation is generally found in various blends and has been reported to be due to the softening or diluting effect of the component [19-11,13]. The presence of POEgMAH rubber, which is more elastic, appears to override the stiffening effect of PA6 and organoclay. A gradual drop in flexural strength and flexural modulus were observed with the incorporation of 10 wt% POEgMAH, but the decline of properties were more significant with further addition of POEgMAH.



**Figure 1: Effect of POEgMAH content on flexural strength and flexural modulus of PA6/PP nanocomposites**



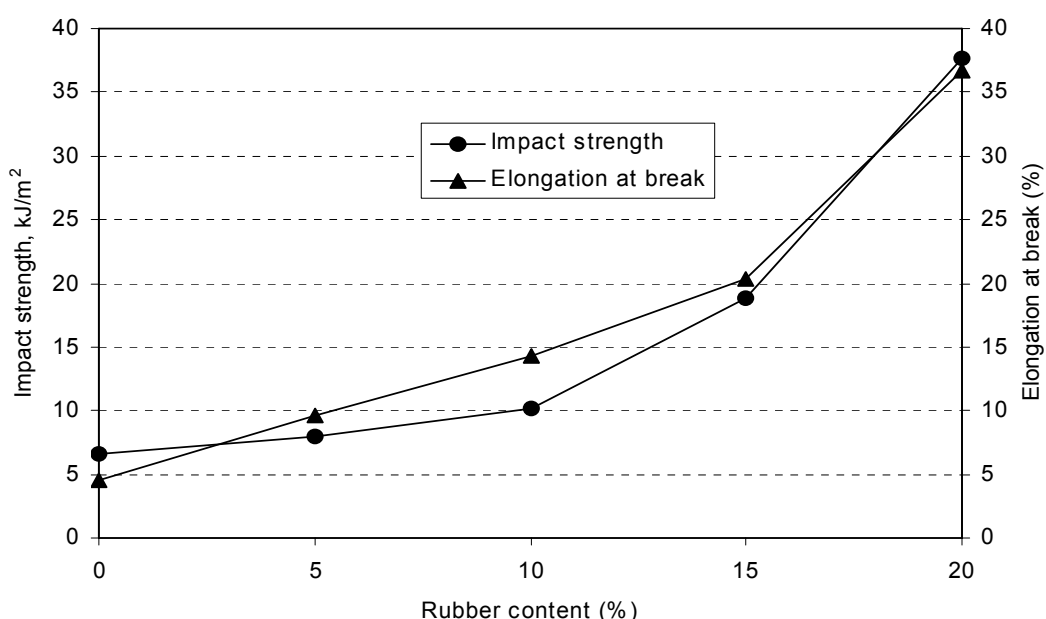
**Figure 2: Effect of POEgMAH content on tensile strength and Young's modulus of PA6/PP nanocomposites**

As shown in Figure 3 the impact strength and elongation at break of PA6/PP nanocomposites increased steadily with increasing rubber content. These results revealed that the incorporation of POEgMAH copolymer phase has substantially improved toughness and elongation at break of PA6/PP nanocomposites. The impact strength increased greatly from 6.65 kJ/m<sup>2</sup> in un-toughened PA6/PP nanocomposites to 37.6 kJ/m<sup>2</sup> after 20 wt% POEgMAH was added into PA6/PP nanocomposites. Yu *et al.* [14] reported that with increasing POEgMAH content up to 30 wt%, extensive cavitation of the rubber particles and matrix shear yielding can be seen through

fracture topography, which led to a large amount of plastic deformation thereby dissipating a significant amount of impact energy. It was reported that blends containing 30 wt% POEgMAH exhibited the highest impact strength.

Bai *et al.* [10] also reported that the toughness of PP/PA6/POEgMAH blends increased with alloying content (PA6+POEgMAH with ratio 2:1). As increasing alloying content, the POEgMAH interlayer (encapsulating the PA6) is thick and PA6 particles are highly elongated which result in higher notched impact strength and rough fracture surfaces.

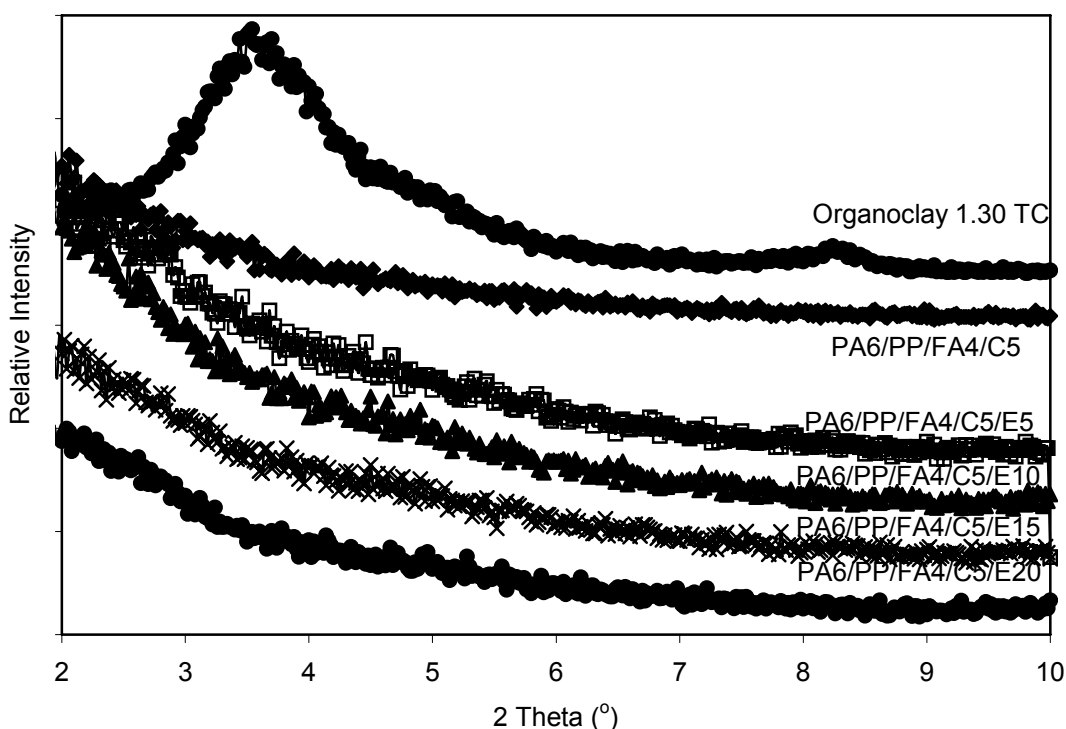
According to Gonzalez-Montiel *et al.* [9] there are 2 ways in which rubber content may affect blends toughness. Firstly an increase in rubber content might increase the volume fraction of the rubber dispersed in the PA. Secondly increasing rubber content might promote the generation of more rubber/PA graft copolymer, which contributed to an improved dispersion of the PP phase. They suggested that 15 % EPRgMAH rubber is sufficient to achieve toughness for all over range of PA6/PP at room temperature.



**Figure 3: Effect of POEgMAH content on impact strength and elongation at break of PA6/PP nanocomposites**

Figure 4 shows the XRD patterns in the range of  $2\theta = 2-10^\circ$  for organoclay, and the nanocomposites of PA6/PP blends. It can be seen from Figure 4 the XRD patterns of the organoclay 1.30 TC exhibited a broad intense peak at around  $2\theta = 3.52^\circ$  corresponding to a basal spacing of 2.48 nm. The XRD pattern of the PA6/PP blends nanocomposites (with 30 % weight fraction of PP) was similar to PA nanocomposites reported previously, where no diffraction peak was detected [1-5]. This result indicates that the organoclay were delaminated

Figure 4 shows the effect of POEgMAH elastomer concentration on XRD patterns of PA6/PP nanocomposites containing 4 wt% organoclay and 5 wt% PPgMAH. It can be seen that no diffraction peak detected for all POEgMAH concentration. The absence of the characteristic clay  $d_{001}$  peak in toughened PA6/PP nanocomposites is an evidence for the formation of exfoliated nanocomposites. Dasari *et al.*[15] were obtained similar result and suggested that the organoclay is fully exfoliated in the presence of SEBSgMAH in PA6/SEBSgMAH/organoclay nanocomposites. These results also imply that POEgMAH concentration was not affect the organoclay dispersion in the formation of the intercalated or exfoliated structure.



**Figure 4: XRD patterns for PA6/PP nanocomposites containing POEgMAH from 0-20 wt%**

## CONCLUSION

The effect of the incorporation of POEgMAH on the mechanical properties and morphology of PA6/PP nanocomposites have been investigated. Significant changes in blend morphology and mechanical properties were obtained when POEgMAH was employed. Addition of POEgMAH to PA6/PP nanocomposites resulted in a drop in tensile and flexural properties whereas the impact strength increased significantly. Addition of 20 wt% POEgMAH increased the impact strength by 500% but decreased the flexural modulus 60% compared to untoughened PA6/PP nanocomposites. XRD evidenced that organoclay were exfoliated with the incorporation of POEgMAH.

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